# Monte Carlo study of the Widom-Rowlinson fluid using cluster methods

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### Abstract

The Widom-Rowlinson model of a fluid mixture is studied using a new cluster algorithm that is a generalization of the invaded cluster algorithm previously applied to Potts models. Our estimate of the critical exponents for the two-component fluid are consistent with the Ising universality class in two and three dimensions. We also present results for the three-component fluid.

Some years ago Widom and Rowlinson [1] introduced a simple but non-trivial continuum model that exhibits a phase transition [2]. The two-component formulation of this model consists of "black" and "white" particles; particles of the same type do not interact, but particles of differing type experience a hard-core repulsion at separations less than or equal to  $\sigma$  [3]. In this letter we present a new Monte Carlo method for simulating the Widom-Rowlinson (WR) model and apply the method to study the properties of the transition point in two and three dimensions.

There have been relatively few Monte Carlo studies of the WR critical point because of the combined difficulties of treating hard-core systems and critical slowing down using standard Monte Carlo techniques. The algorithm presented here overcomes these difficulties by using a generalization of the cluster approach introduced by Swendsen and Wang [4]. The algorithm is a variant of the invaded cluster (IC) method [5,6] adapted to continuum problems. We find that the algorithm has almost no critical slowing down and that we can obtain accurate values of the critical density and the exponent ratios  $\beta/\nu$  and  $\gamma/\nu$  with relatively modest computational effort.

The 2-component WR model is expected to be in the Ising universality class. Our results for  $\beta/\nu$  and  $\gamma/\nu$  are consistent with this assumption and are in good agreement with the best known values for the Ising model. Our value for the critical density of the three-dimensional (d=3) WR model agrees with recent results obtained by Shew and Yethiraj [7].

We also consider a WR model in which there are q components, any two of which interact via a hard-core repulsion. Despite the apparent similarity to the q-state Potts model, the phase structure may have additional features [8,9]. Our algorithm easily extends to these q-component WR models, and we present results for the 3-component model in d = 2, 3.

Graphical Representations of the WR Model. A configuration of the WR fluid consists of two sets of points, S and T, corresponding to the positions of the black and white particles respectively. In the grand canonical ensemble, the probability density for finding the configuration (S,T) is

$$P(S,T) = \frac{1}{Z} \frac{z_1^{N_1}}{N_1!} \frac{z_2^{N_2}}{N_2!} \Gamma(S,T).$$
 (1)

 $\mathcal{Z}$  is the grand partition function,  $z_1$  ( $z_2$ ) is the fugacity of the black (white) particles, and  $N_1$  ( $N_2$ ) is the number of black (white) particles. The object  $\Gamma$ , which expresses the hard-core interaction between particles of different types, vanishes if any point in S is within a distance  $\sigma$  of any point in T and is one otherwise. Symmetry considerations insure that the critical point is along the line  $z_1 = z_2$ ; hereafter we restrict attention to the case,  $z = z_1 = z_2$ .

To motivate and justify our cluster algorithm, we consider a different representation of the WR model. In the "gray" representation [10,11] one considers the particles without reference to color, but with configurations weighted according to the number of allowed colorings. Let W be a list of N points,  $W \equiv (\mathbf{r}_1, \dots \mathbf{r}_N)$ . Clusters of particles can be defined by the condition that every particle in a cluster is within a distance  $\sigma$  of some other particle in the cluster. Particles in a cluster must all be the same color, so if there are C(W) distinct clusters (including single particles), there are  $2^{C(W)}$  allowed colorings. Starting with Eq. (1) and working through the combinatorics, we find that the probability density for W is given by

$$p(W) = \frac{1}{Z} \frac{z^N}{N!} 2^{C(W)}.$$
 (2)

These densities describe the gray measures. The appropriate gray measure for the q-component model is defined by the analog of Eq. (2) with 2 replaced by q. To return to the distribution in Eq. (1) starting from the gray representation, we select one of the  $2^{C(W)}$  (or  $q^{C(W)}$ ) allowed colorings with equal probability. It turns out that the gray measures are a special case of the models studied in [12]. The connection with the WR models was discussed in [13] and made precise in [10,11].

Cluster Algorithms. With the gray representation in mind, we consider the following cluster algorithm. Starting from a configuration W of gray particles, clusters are identified. Each cluster is independently labeled black or white with probability 1/2 and all the white particles are removed. In the next step, white particles are replaced via a Poisson process

at fugacity z in the free volume permitted by the black particles. In the final step, color identities are erased and we obtain the next gray configuration. The generalization to the q-component WR model is that the fraction of clusters deleted is 1/q. This algorithm is the generalization of the Swendsen-Wang method to the WR model. The algorithm is described in more detail and detailed balance is proved in [14] and independently in [15].

Because we are interested in efficiently sampling the transition point of WR models, we will forsake a Swendsen-Wang approach in favor of an IC algorithm. The steps involving the coloring and discarding of clusters are essentially the same, but rather than repopulating the free volume by a fixed fugacity process, particles are sequentially added with a uniform distribution throughout the free volume until a *stopping condition* is fulfilled. For example, one could add particles until a fixed particle number is reached. If a stopping rule is chosen that enforces a condition which is characteristic of criticality, then a critical state of the system is sampled automatically. In a finite volume the IC method samples an ensemble that differs from the canonical ensemble, but it presumably converges to the correct infinite volume distribution for all local observables. The validity of the IC method and its relation to the Swendsen-Wang method is discussed briefly below and in detail in Ref. [6].

The signature of the phase transition in the WR model is percolation of a gray cluster [10,11]. Thus an appropriate stopping rule for the IC algorithm is the spanning of a gray cluster – particles are added at random in the allowed volume until a cluster spans the system. (In our case, we use periodic boundary conditions and spanning is said to occur when a cluster wraps the torus.) The other modification is that the spanning cluster is erased on each deletion move, thereby ensuring that a new spanning cluster can form in the repopulation move.

If  $N_{\rm tot}$  denotes the total number of points that are needed to satisfy the stopping condition, then  $z=N_{\rm tot}/V$  is an estimator for the critical fugacity  $z_c$ . In the limit  $V\to\infty$ , it is reasonable to assume that the distribution for z becomes sharp. If this assumption is valid, each move is identical to a move of the Swendsen-Wang-type algorithm at the peak value of z. It follows that this peak value is  $z_c$  – no other value of the fugacity would exhibit

a critical cluster. Hence, if the distribution for z is very narrow in a finite volume, the IC algorithm is essentially the Swendsen-Wang-type algorithm with small fluctuations in the fugacity.

Results. We now present our simulation results using the IC method. We collected statistics for the following quantities: the average number of particles in the spanning cluster, M; the normalized autocorrelation function  $\Gamma_M(t)$  of the number of particles in the spanning cluster as a function of "time" t as measured in Monte Carlo steps; the compressibility  $\chi$  defined by

$$\chi = \frac{1}{V} \sum_{i} s_i^2,\tag{3}$$

where  $s_i$  is the mass of the *i*th cluster and the spanning cluster is included in this sum; the estimator for the critical fugacity  $z = \langle N_{\rm tot} \rangle / V$ ; the fluctuations in z,  $\sigma_z^2 = (\langle N_{\rm tot}^2 \rangle - \langle N_{\rm tot} \rangle^2) / V^2$ ; and the average number of gray particles per unit area (volume)  $\rho$  which is an estimator of the critical density. System size is measured in units of the particle diameter,  $\sigma$ . The results for these quantities are presented in Tables I–IV along with our estimate of the statistical errors.

The critical exponents that depend on the magnetic exponent  $y_h$  can be obtained from the fractal dimension of the spanning cluster via  $M \sim L^D$  or from the compressibility via  $\chi \sim L^{\gamma/\nu}$ . The various critical exponents are related by  $D = y_h$ ,  $\gamma/\nu = 2y_h - d$ , and  $\beta/\nu = d - y_h$ . The dynamical properties of the algorithm can be measured by the integrated autocorrelation time defined by  $\tau_M = \frac{1}{2} + \sum_{t=1}^{\infty} \Gamma_M(t)$ . The integrated autocorrelation time is roughly the number of Monte Carlo steps between statistically independent samples and enters into the error estimate for M. In practice, it is necessary to cut off the upper limit of the sum defining  $\tau_M$  when  $\Gamma_M$  becomes comparable to its error. The increase in  $\tau_M$  defines a dynamic exponent  $z_M$  via  $\tau_M \sim L^{z_M}$ .

Our results for the 2-component, d=2 WR fluid are summarized in Table I. From the log-log plot of M versus L shown in Fig. 1, we find that  $y_h=d-\beta/\nu=1.873\pm0.002$ , and hence  $\beta/\nu\approx0.127$ , a value consistent with the exact Ising result of  $\beta/\nu=1/8$ . Similarly, a

log-log plot of  $\chi$  versus L yields  $\gamma/\nu = 1.743 \pm 0.003$ , consistent with the exact Ising value,  $\gamma/\nu = 7/4$ . These results support the hypothesis that the 2-component d=2 WR fluid is in the Ising universality class. The errors quoted here are associated with the least squares fitting procedure and are two standard deviations. We also estimated the statistical errors in  $y_h$  and  $\gamma/\nu$  by generating synthetic data sets consistent with the estimated errors in the measured values of M and  $\chi$  and found similar results.

From the data of Table I we have estimated the infinite volume critical values of the density,  $\rho_c$  and fugacity,  $z_c$ . A linear fit for  $\rho(L)$  versus 1/L yields  $\rho_c = 1.5652$ . A three parameter fit of the form

$$\rho(L) = \rho_c - A/L^x,\tag{4}$$

yields  $\rho_c = 1.5662$  with x = 0.96. Because the biggest source of error is the uncertainty in the fitting form rather than the statistical errors in the raw data, we estimate the error in  $\rho_c$  as several times the difference between these two fits. Hence, we conclude that  $\rho_c = 1.566 \pm 0.003$ .

Within the statistical error the fugacity z is unchanged for the three largest system sizes. We take these values and several times the statistical error to estimate the critical fugacity,  $z_c = 1.726 \pm 0.002$ . To our knowledge, there are no independent estimates of  $\rho_c$  and  $z_c$  for the 2-component, d = 2 WR fluid.

The autocorrelation function,  $\Gamma_M(t)$  decreases rapidly and oscillates about zero after  $t \approx 10$ . Our results for  $\tau_M$  for various system sizes are summarized in Table I. The slow increase of  $\tau_M$  with L indicates that the dynamic critical exponent  $z_M$  is small or zero  $(\tau_M \sim \ln L)$ . Because of its small value and our limited data, we cannot make a more precise statement. Fitting  $\Gamma_M(t)$  to a single exponential leads to decorrelation times similar to the integrated autocorrelation time.

Our results for the 2-component, d=3 WR fluid are summarized in Table II. Power law fits of M and  $\chi$  versus L yield  $y_h=3-\beta/\nu=2.479\pm0.001$  and  $\gamma/\nu=1.961\pm0.003$ , respectively. These values are consistent with each other and with the recent estimate of

 $y_h = 2.4815(15)$  obtained in Ref. [16]. The results confirm the expectation that the 2-component, d = 3 WR model is in the d = 3 Ising universality class.

In Fig. 2 we show  $\rho$  versus 1/L. A linear fit yields  $\rho_c = 0.7484$ . A three parameter fit of the form given in Eq. (4) yields  $\rho_c = 0.7478$  with x = 1.16. We estimate the error in  $\rho_c$  as several times the difference between these two fits and conclude that  $\rho_c = 0.748 \pm 0.002$ . This value of  $\rho_c$  is in agreement with and improves upon the recent result in Ref. [7],  $\rho_c = 0.762 \pm 0.016$ . These values for  $\rho_c$  are much higher than older estimates of  $\rho_c$  which were in the range of 0.41 to 0.57 [17].

From the estimates of  $\tau_M$  shown in Table II, we see that  $\tau_M$  does not appear to increase with L. It may be that there is no critical slowing for IC dynamics for the 2-component, d = 3 WR model as is the case for the d = 3 Ising model under IC dynamics [6,18].

The fluctuations in the estimator of the fugacity,  $\sigma_z$ , decrease with L as  $\sigma_z \sim L^{-a}$  with  $a \approx 0.5$  for d=2 and  $a \approx 0.8$  for d=3. The d=2 value of a is the same as was found for the d=2 Ising model in the IC ensemble while for d=3 it is somewhat larger than the results obtained for the d=3 Ising model [18] where  $a=0.69\pm0.01$ . The fact that  $\sigma_z \to 0$  as the system size increases insures that the IC ensemble is close to the canonical ensemble.

Our results for the 3-component WR fluid in d=2 are summarized in Table III. Using the same finite size scaling analysis we used for the 2-component WR fluid, we find that  $D=y_h=1.842\pm0.004$  and hence  $\beta/\nu\approx0.16$ . This result for  $y_h$  is consistent with our observed value of  $\gamma/\nu=1.681\pm0.008$ . These results are not consistent with the corresponding value for the 3-state, d=2 Potts model where  $y_h=28/15$ . Even more surprising, our estimated value of  $y_h$  for the WR fluid is less than the minimum value of  $y_h$  for any d=2 Potts model with a continuous transition ( $y_h\approx1.86603$  for q=3.332). This observation deserves further study. Is the 3-component, d=2 WR fluid outside the Potts universality classes or are the systematic errors considerably larger than we have guessed?

We also find that  $\rho$  approaches  $\rho_c$  as 1/L and extract the value  $\rho_c = 1.657 \pm 0.001$ . The standard deviation of the estimator of the fugacity decreases as  $\sigma_z \sim L^{-0.4}$ . A log-log plot of  $\tau_M$  versus L yields the estimate of the dynamic exponent  $z_M = 0.58$ , that is, for this case

z is sufficiently large for us to conclude that z > 0.

Our results for the 3-component, d=2 WR fluid are summarized in Table IV. The corresponding 3-state, d=3 Potts model is believed to have a first-order transition, and it is likely that this behavior holds for the 3-component d=3 WR fluid. On the other hand, both the observed values of M and  $\chi$  are well-described by power laws. This situation also holds for the 3-state Potts model for computationally accessible system sizes and reflects the fact that the transition is very weakly first-order. More study is needed to determine the order of the transition for this case of the WR model. The IC method finds the transition temperature for Potts models independently of whether the transition is first-order or continuous [6]. Hence, we believe that extrapolated values of z yields the transition value of the fugacity,  $z_c \approx 1.16$ , and that  $\rho \approx 0.795$  lies between the density of the two co-existing phases at the transition. The standard deviation of the fugacity decreases with L as  $\sigma_z \sim L^{-0.25}$ . The effective dynamic exponent describing the increase in  $\tau_M$  is  $z_M=0.62$ .

We have shown that cluster methods may be effectively used to study the Widom-Rowlinson model. To our knowledge, the IC algorithm is the first example of an algorithm that performs efficiently near the critical point of a continuum system with hard-core interactions. We have obtained accurate values of the critical density and fugacity for Widom-Rowlinson models in d=2 and 3. The 2-component Widom-Rowlinson model appears to be in the Ising universality class. However, the 3-component d=2 model deserves further study and might not be in the 3-state Potts universality class.

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**TABLES** 

TABLE I. Dependence of M,  $\rho$ ,  $\chi$ , z,  $\sigma_z$ , and  $\tau_M$  on L for the 2-component, d=2 WR fluid. The error estimates represent one standard deviation. The averages are over  $10^5$  spanning clusters.

L	M	ho	χ	z	$\sigma_z$	$ au_M$
40	1511(1)	1.5247(4)	1584(2)	1.7201(7)	0.212	0.58
60	3233(3)	1.5379(3)	3217(5)	1.7247(6)	0.170	0.60
80	5527(5)	1.5450(3)	5289(9)	1.7267(6)	0.150	0.72
120	11836(12)	1.5516(3)	10760(20)	1.7265(5)	0.120	0.78
160	20282(20)	1.5552(2)	17752(30)	1.7262(4)	0.101	0.77

TABLE II. Dependence of M,  $\rho$ ,  $\chi$ , z,  $\sigma_z$ , and  $\tau_M$  on L for the 2-component, d=3 WR fluid. The averages are over  $10^6$  spanning clusters.

L	M	ρ	χ	z	$\sigma_z$	$ au_M$
10	313.0(1)	0.74022(7)	119.5(2)	0.9387(1)	0.138	0.59
20	1745.4(6)	0.74440(4)	466.1(9)	0.940(1)	0.077	0.57
30	4768(2)	0.74567(2)	1031(2)	0.9403(1)	0.056	0.57

TABLE III. Dependence of M,  $\rho$ ,  $\chi$ , z,  $\sigma_z$ , and  $\tau_M$  on L for the 3-component, d=2 WR fluid. The averages are over  $10^5$  spanning clusters.

L	M	ho	χ	z	$\sigma_z$	$ au_M$
40	1480(2)	1.6124(8)	1543(4)	1.965(3)	0.364	0.88
80	5325(7)	1.6352(6)	4987(13)	1.960(1)	0.280	1.2
120	11211(18)	1.6418(6)	9810(30)	1.953(1)	0.237	1.7
160	19013(32)	1.6455(6)	15869(50)	1.949(1)	0.213	1.9

TABLE IV. Dependence of M,  $\rho$ ,  $\chi$ , z,  $\sigma_z$ , and  $\tau_M$  on L for the 3-component, d=3 WR fluid. The averages are over  $10^5$  spanning clusters.

L	M	ho	χ	z	$\sigma_z$	$ au_M$
10	299.6(3)	0.7914(2)	109.8(2)	1.1789(8)	0.230	0.58
20	1639(2)	0.7947(2)	409.1(9)	1.1717(6)	0.145	0.74
30	4407(6)	0.7947(1)	874(2)	1.1670(5)	0.117	0.83

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## FIGURES

- FIG. 1. Log-log plot of M, the average mass of the spanning cluster, versus L, the linear dimension of the lattice for the 2-component, d=2 WR fluid. A least squares fit yields  $D=2-\beta/\nu=1.873.$
- FIG. 2. Plot of  $\rho$  versus 1/L for the 2-component, d=3 WR fluid. A least squares fit yields  $\rho_c=0.7484.$



